ISOLATION OF VINCANINE

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Vincanine has been isolated from the roots of Vinca erecta Rgl. et Schmalh. [1]. The content of vincanine in the roots varies from 0.5 to 0.9%. The hydrochloride of this substance is an analeptic for the central nervous system [2, 3]. We have investigated the possibility of extracting vincanine from roots with weak solutions of acids (sulfuric, hydrochloric, acetic) and water. Good results have been obtained with the use of a 1% solution of acetic acid. Of the cation exchangers KU-1, KU-2, and KB-4P-2, KU-1 possesses the greatest exchange capacity with respect to the combined alkaloids of the roots. The extraction process was carried out continuously in a battery of four extractors combined in series by the flow method. A 1% solution of acetic acid was passed at the rate of 5 *l*/hr. 40 *l* of extract was run off from the first extractor, and then the last extractor was disconnected, and one containing fresh roots was placed in place of the first extractor. In this way more than 100 kg of roots was extracted.

The extract was filtered and passed through a battery of absorbers consisting of three columns with 4.2 kg of ion-exchanger (air-dry) in each. The total thickness of the layer of ion-exchanger was 0.4 m × 3 = 1.2 m. No alkaloids could be detected in the solution taken from the third absorber. A 1.5% solution of ammonia in 85% ethyl alcohol proved to be a good desorbent.

The alcoholic solution obtained from the absorbers was concentrated in vacuum to half bulk and was acidified with concentrated hydrochloric acid. The acidified eluate was evaporated until the alcohol had been completely eliminated. About 17 *l* of the acid solution (residue after the extraction of 100 kg of roots) was made alkaline with an excess of 30% caustic soda (to convert the phenolic alkaloid vincanidine into the phenoxide, which is sparingly soluble in chloroform) and was extracted three times with chloroform. The latter was distilled off to dryness in vacuum and the vincanine was isolated by treating the dry residue with acetone. From this base vincanine hydrochloride was obtained.

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GENERAL METHOD OF OBTAINING 5'-O-(α-ALKOXYALKYL)-DERIVATIVES OF NUCLEOTIDES

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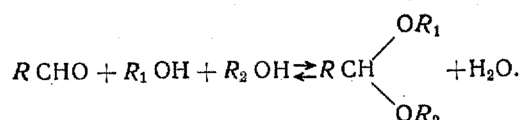
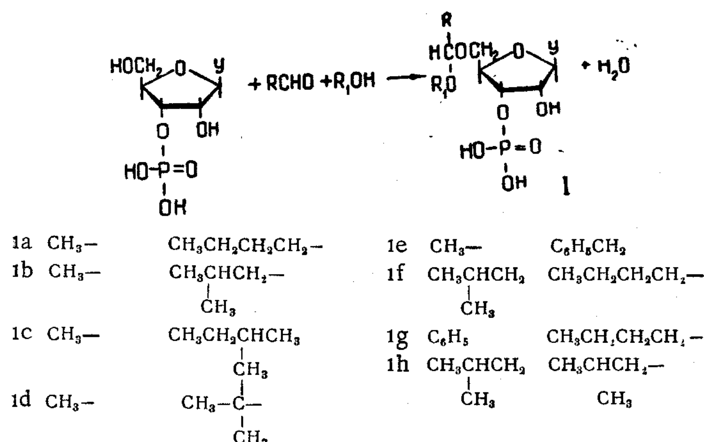
We have previously reported that 5'-O-(α-butoxyethyl) uridine 3'-phosphate [1, 2] and 2'-O-(α-ethoxyethyl)-5)-O-acetyluridine 3'-phosphate [3] are of interest as intermediates in the synthesis of oligonucleotides. These compounds were obtained by the treatment of uridine 3'-phosphate and 5'-O-acetyluridine 3'-phosphate, respectively, with vinyl butyl ether and vinyl ethyl ether, respectively.

In the present paper we propose the use, as a more general method of synthesis of 5'-O-(α-alkoxyalkyl) derivatives of nucleotides, of the reaction for obtaining mixed acetals from an aldehyde and a mixture of alcohols [4].



$$RCHO + R_1OH + R_2OH \rightleftarrows RCH(OR_1)(OR_2) + H_2O.$$

In order to show the applicability of this reaction to the case under consideration, when one of the alcohols is the carbohydrate part of a nucleotide, we have synthesized 5'-O-(α-butoxyethyl) uridine 3'-phosphate (Ia) by treating uridine 3'-phosphate with an excess of acetic anhydride and butan-1-ol in the presence of anhydrous alumina at 15° C for 6–7 hr. Under these conditions about 28% of 5'-O-(α-butoxyethyl) uridine 3'-phosphate is formed together with traces of 2', 5'-O, O-di-(α-butoxyethyl) uridine 3'-phosphate. The 5'-O-(α-butoxyethyl)-uridine 3'-phosphate was isolated from the reaction mixture by means of chromatography on cellulose powder; the solvent was a mixture of isopropanol, concentrated ammonia, and water (7 : 1 : 2). This substance proved to be identical with the 5'-O-(α-butoxyethyl) uridine 3'-phosphate prepared by our previous method [1] by its partition coefficient in paper chromatography with the solvent isopropanol– conc. ammonia– water (7 : 1 : 2), with respect to its mobility on paper electrophoresis in a 0.05 M solution of triethylammonium hydrogen carbonate, by its behavior in 2 N acetic acid, and by its IR spectrum. 5-O-(α-Alkoxyalkyl) derivatives of uridine 3'-phosphate with other aldehydes and alcohols – (Ib)-(Ih) have also been obtained.



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SPECIFIC ALKYLATION OF CHYMOTRIPSIN WITH THE AZIDE OF THE S-CARBOXYMETHYLMERCAPTIDE OF p-MERCURIBENZOIC ACID

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We have studied the acylation of chymotripsin with the azide of the S-carboxymethylmercaptide of p-mercuribenzoic acid [1]. Chymotripsin was treated in an acetate buffer (pH 5.0) with a large excess of the azide at 2° C for 36 hr, after which the enzyme had lost its esterase activity as determined by the hydrolysis of p-nitrophenyl acetate. The low-molecular-weight components of the mixture were eliminated by gel filtration on Sephadex G-25 equlibrated with 0.002 N hydrochloric acid; then the acylated enzyme was freeze-dried.

A determination by the dithizone method showed that the molecule of the acyl-enzyme contained one atom of mercury. The treatment of the acyl-enzyme with hydroxylamine at pH 6.0 led to the cleavage of 1 mole of hydroxamate from 1 mole of acyl-enzyme. The acylated chymotripsin was completely reactived after incubation for 20 hr at pH 5.0 or 2 hr at pH 6.0.

The selective acylation and the high reactivity of the bond formed permit the assumption that it is the active hydroxyl of serine located in the catalytic center of chymotripsin that reacts with the azide of the S-carboxymethyl-